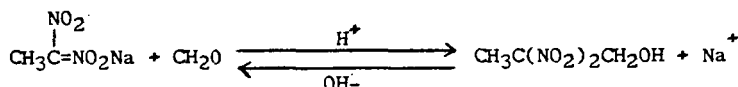


SYNTHESIS OF 2,2-DINITROPROPANOL.
STUDIES ON CONTINUOUS PREPARATION

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A program was undertaken to investigate various methods of preparing the 2,2-dinitropropanol (I), with the ultimate objective of developing a process suitable for large scale production. With the exception of one synthetic route, which will be discussed later, the key step in the synthesis of I is the preparation of 1,1-dinitroethane (II) or its nitronate salt. The conversion of II to I is straightforward using the method of Henry¹ in which an aqueous suspension of the dinitroparaffin is treated with formaldehyde in the presence of a basic catalyst. In practice, it is usually more convenient to start with the nitronate salt of the dinitroparaffin and add one equivalent of acid to the solution:



The product is isolated by extraction with a solvent followed by removal of the solvent in vacuo to leave I in the form of a waxy white solid. The material prepared in this manner is of satisfactory purity for use as an intermediate in most reactions without further purification. Analytically pure I can be prepared by repeated sublimation in vacuo; it is quite hygroscopic when pure and its melting point (92-94°) is extremely susceptible to depression by small amounts of impurities.

At the outset of this work, two routes to II were known which appeared sufficiently attractive for investigation as potential production processes.

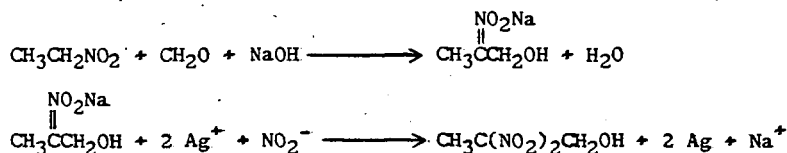
OXIDATIVE-NITRATION REACTION

The most convenient method for preparing gem-dinitro compounds involves the reaction discovered by Kaplan and Shechter² in which treatment of the nitronate salt of a primary or secondary mononitroparaffin with silver nitrate and an inorganic nitrite in aqueous media gives the corresponding gem-dinitro compound and metallic silver:

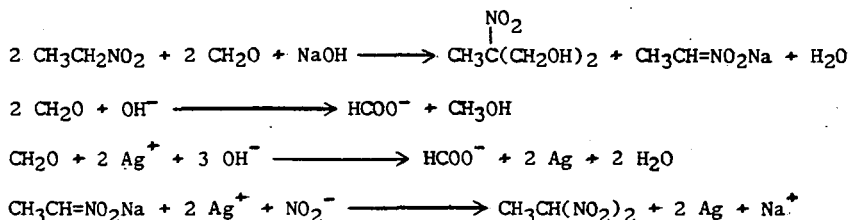


The reaction, which has been termed an oxidative-nitration process, has been used to prepare a variety of primary, secondary, and functionally substituted dinitroparaffins. The silver produced in the reaction may be separated and converted to aqueous silver nitrate by treatment with concentrated nitric acid; after pH adjustment of the resulting solution to 5-6, it is ready for re-use.

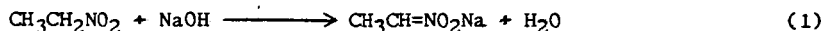
The preparation of I by this procedure was initially carried out in these laboratories via the intermediate sodium 1-hydroxy-2-propanenitronate, which in turn was prepared by treatment of a suspension of nitroethane in aqueous formaldehyde with sodium hydroxide:



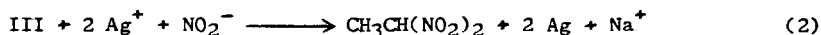
Overall yields of 65-70% (corrected for the purity of commercial grade nitroethane) were obtained. Principal drawbacks to this procedure were side reactions which could be suppressed, but not eliminated, by careful control of reaction variables:



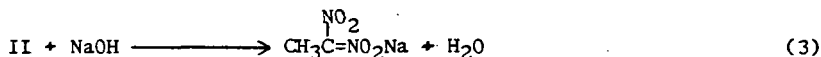
To circumvent these side reactions, a modified procedure was developed in which the oxidative-nitration was carried out before the methylation step:



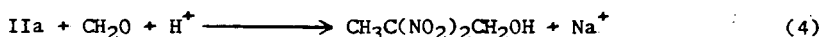
III



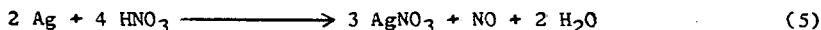
II



IIa



I



Under the conditions described below, laboratory yields in reactions 1-4 were approximately 98, 90, 98, and 97% respectively. With a 95% extraction recovery of I from the aqueous layer, this gives an overall yield of 80% based on nitroethane. A typical analysis of material produced by this method is given in Table 1. Reaction 5 is essentially quantitative and losses in this step are primarily mechanical; silver losses will be discussed later in this section. Reaction 1 was carried out at 0-10° in most instances, although temperatures up to 20° could be used without noticeable change in results; at temperatures above ambient, side reactions leading to trimethylisoxazoles become appreciable.³ Using a 5-10% excess of sodium hydroxide, added with vigorous agitation to the nitroethane-water suspension, the reaction was complete within 10 minutes after completion of addition of the base. At this point, sodium nitrite was added and the resulting solution (at 0-10°) was added rapidly to a vigorously stirred solution of the silver nitrate maintained at -5 to

0°. As reaction 2 proceeded, a solid (presumably an intermediate complex²) separated and the mixture became extremely thick, then progressively less viscous as metallic silver separated; the reaction is accompanied by an exotherm, and external cooling was applied as required to keep the temperature below 20°. When the exotherm was over, 50% sodium hydroxide was added over a 15-minute period at 15-20° to convert II to its water soluble sodium salt (reaction 3) and to precipitate excess silver ion as silver oxide. After filtration and water washing of the silver, the pH of the combined filtrates was reduced to 9-10 with acetic acid; a 10% excess of 37% formaldehyde was then added and the acidification was continued until a pH of 5.0-5.5 was reached (reaction 4). The aqueous solution, containing 7-9% of I was then extracted with ethylene chloride either batchwise or in a countercurrent column. Extraction efficiencies of 94-96% were attained. The ethylene chloride solution of I was then concentrated in vacuo to the desired strength prior to use as an intermediate in subsequent reactions. The metallic silver recovered from the oxidative-nitration step was converted to silver nitrate by slurrying in water and treatment with a slight excess of 67% nitric acid at 30-40°. The pH of the resulting solution was then adjusted to 5-6 with sodium hydroxide; some silver oxide was formed in this step, but did not interfere with use of the solution in a subsequent oxidative-nitration, since the oxide is also converted to silver in the reaction.

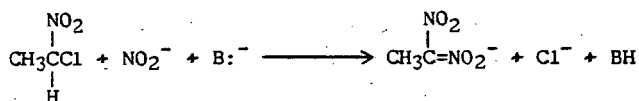
The procedure was adapted to batch pilot plant operation using 0.5 lb mole of nitroethane, and was eventually increased to a 2.0 lb mole scale. Although the overall yields on the pilot plant scale averaged about 5% lower than those obtained in laboratory preparations, the process presented no major scale-up problems. In initial pilot plant studies, silver was recovered by centrifuging the slurry after the neutralization step in which II was converted to its soluble sodium salt. In order to reduce silver losses due to handling, internal stainless steel filters were subsequently installed in the oxidative-nitration reactor and the slurry was pressure filtered rather than centrifuged. Using this procedure, the silver was not removed from the kettle from run to run; after filtration and washing, the silver was slurried with water and nitric acid was added to regenerate silver nitrate. Handling losses were reduced considerably and would have been reduced further had it not been for the occasional formation of very finely divided silver in the reaction. When this occurred, filtration was extremely slow and it was necessary to allow the slurry to settle, after which the supernatant liquid could be removed by siphoning. Subsequent washing of the silver was difficult and inefficient, and silver losses occurred despite filtration of the siphoned material. The cause of fine silver formation was not determined but appeared to be associated with the buildup of small quantities of organic material in the silver. Thus, once finely divided silver had formed, the problem was greatly magnified since it was difficult to wash the silver adequately, and the buildup of organic material in the silver cake increased rapidly in subsequent runs. It has been our experience that the best way to avoid this difficulty is to maintain a uniform dispersion of silver in the mixture by providing excellent agitation during the oxidative-nitration, neutralization, and silver washing steps.

Several hundred thousand pounds of I were produced by the oxidative-nitration method at this facility. Under normal operating conditions, silver losses averaged about 1%. Over short periods of time, losses ran as low as 0.5% and as high as 2%. The 1% loss can be tolerated for the preparation of development quantities of I but becomes a serious drawback for larger scale production. Other economic disadvantages to the process are the required use of expensive low-chloride grade sodium hydroxide (to avoid formation of silver chloride) and the relatively large quantities of nitric acid required to regenerate silver nitrate from recovered silver. A study of an alternate procedure, not requiring the use of silver nitrate, was therefore undertaken. It should be mentioned that a modification of the oxidative-nitration has been described recently⁴ in which the reaction is carried out in an electrolytic cell, with silver ion being regenerated as it is consumed. While this procedure

shows promise of overcoming the problem of silver losses, a considerable amount of development work remains to be done before its ultimate potential for large scale production is known.

TER MEER REACTION

An alternate method for preparing salts of terminal gem-dinitro compounds that has been known for many years is the ter Meer reaction,⁵ and involves treatment of 1-halo-1-nitroparaffins with nitrite ion in basic media to give the anion of the terminal gem-dinitro compound and chloride ion. In the case of 1-chloro-1-nitroethane the reaction is:



In practice it is desirable (by suitable choice of reaction solvent and/or metal cation) to force separation of the nitronate anion from the reaction mixture as a sparingly soluble salt as it is formed. In this manner, side reactions are suppressed and the reaction is driven to completion. Potassium ion is the cation of choice since potassium 1-nitro-1-ethanenitronate is sparingly soluble in water and essentially insoluble in most organic solvents; the sodium salt may be employed satisfactorily in nonaqueous systems but gives poor results in aqueous media, presumably due to its high solubility. The most commonly used solvents for the reaction are water, alcohol, or water-alcohol mixtures. The choice of base in the reaction is important. Strong bases, such as alkali metal hydroxides, give only fair results since they readily attack the 1-halo-1-nitroparaffin to give not only the nitronate salt but side reaction products resulting from cleavage of both C-NO₂ and C-Cl bonds. Extremely weak bases result in slow rates and incomplete reaction. Best results have been obtained using carbonates or, specifically, potassium carbonate. Reaction temperatures of 0-25° and times of 30-120 minutes are generally used; good agitation is essential to high conversions since the reaction system is heterogeneous regardless of the solvent employed. The product, potassium 1-nitro-1-ethanenitronate, is usually purified by filtration and washing with methanol to remove organic impurities which are adsorbed on the salt. This operation is undesirable inasmuch as the potassium salt, when dry, is quite sensitive to detonation by shock. It has a 50% fire point of less than 5 cm using a 2 kg weight in the Bureau of Mines impact tester (about the same as nitroglycerin). The material may be handled safely, provided it is kept wet with water or an organic solvent. The degree of improvement in impact stability depends upon the amount and nature of the solvent; water or aqueous alcohol is quite effective in amounts in excess of 30% based on the weight of the dry salt. The salt is easily converted to the dinitro-alcohol, I, by treatment with aqueous formaldehyde and acid as described in the previous section.

The ter Meer route to I was investigated at these facilities several years ago, both on a laboratory and small pilot plant scale. The best grade of 1-chloro-1-nitroethane available at the time in the quantities required was material of 80% purity. It also contained nitroethane (9.0%), 2-nitropropane (1.2%), 2-chloro-2-nitropropane (3.7%), and 1,1-dichloro-1-nitroethane (6.1%). In the laboratory, overall yields of I ranging from 57-62% (corrected for purity of the starting material) were obtained; the purity of I was acceptable (95-98%) provided the potassium salt of dinitroethane was filtered and washed thoroughly with methanol before proceeding with the methylolation reaction. However, procedures designed to avoid isolation of the hazardous salt on a pilot plant scale gave product of inferior quality. Thus, when the crude product slurry of the potassium salt was treated directly with formaldehyde and sulfuric acid, and the resulting product isolated by solvent extraction and vacuum stripping, product purity was only 85%;

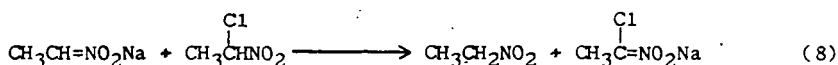
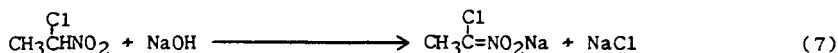
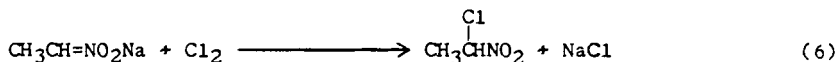
the bulk of the impurities were those present in the original 1-chloro-1-nitroethane. When the aqueous product solution of I was extracted with n-hexane to remove impurities before the ethylene chloride extraction, an improvement in quality to a maximum of about 93% was obtained. In view of these results, and taking into account the cost of 1-chloro-1-nitroethane at the time (\$1.50/lb, available in development quantities only), work on this route to I was discontinued in favor of the oxidative-nitration process. Recently, however, it was shown by other workers⁶ that the method commonly used to prepare 1-chloro-1-nitroethane, namely, the reaction of aqueous sodium ethanenitronate with chlorine, gave a product of considerably improved purity

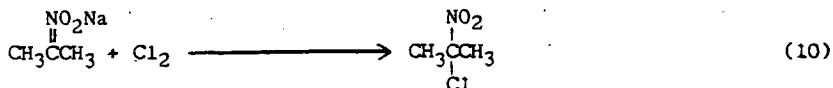
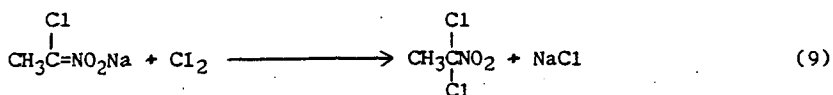


under certain reaction conditions. These results were confirmed and led to a detailed study of the chlorination reaction, as well as to a re-examination of the ter Meer route to I. Emphasis was placed on the development of continuous processes; batch runs were used primarily to outline the most promising conditions for continuous operation.

Preparation of 1-Chloro-1-Nitroethane. The first step in the synthesis, the conversion of the weak acid, nitroethane, to its sodium salt, presents little difficulty by either batch or continuous methods. Nitroethane is simply treated with aqueous sodium hydroxide at 0-10° in a well agitated vessel; in our work it was advantageous to employ concentrations which gave a solution containing approximately 23% of the salt. In batch runs, a sodium hydroxide addition time of 15 minutes and a post addition stirring period of 15 minutes gave excellent results. In continuous runs using the two stage reaction system shown in Fig. 1, a residence time of 45 minutes gave essentially complete conversion. Much shorter reaction times can be employed satisfactorily using extremely vigorous agitation, provided the heat of reaction (approximately 14 kcal/g mole) can be removed from the system. Aqueous sodium ethanenitronate is stable for a minimum of 24 hours at 0-10°; prolonged storage times and/or higher temperatures result in gradual degradation of the salt. The samples of commercial grade nitroethane used throughout these studies had a purity range of 92.8-93.3%; the balance was composed of nitromethane (0.5-1.5%), 2-nitropropane (4-6%) and traces of 1-nitropropane and nitrobutanes. It was found possible to effect a partial purification during sodium salt formation by using an amount of sodium hydroxide exactly equivalent to the nitroethane content of the commercial material. When this was done, a small amount of oil remained on top of the aqueous layer (pH 11.0) after the salt formation reaction was complete. Separation and chromatographic analysis of the oil showed it to contain 90.6% 2-nitropropane, 9.3% nitroethane, and 0.1% nitromethane. The reason for this selectivity of reaction with sodium hydroxide was not investigated but may be due to difference in solubility of 2-nitropropane and nitroethane in water (1.7 and 4.5 ml per 100 ml of water, respectively).

The conversion of the aqueous sodium salt to the chloro derivative was found to proceed extremely fast even at 0°; crude product separated from the reaction mixture as it was formed. The most important reactions occurring in the system are:





Reactions 7, 8, and 9 lead to formation of the byproduct 1,1-dichloro-1-nitroethane. Reaction 7 can be all but eliminated by close pH control of the sodium ethanenitronate feed solution. Reaction 8 can be minimized in batch reactions by using a non-agitated system to reduce contact between the aqueous salt solution and the organic product solution and by removing the product as it is formed; in a continuous system a slight excess of chlorine can be employed. Little can be done to suppress reaction 9, but if conditions are chosen as described above to minimize 7 and 8, there is little sodium 1-chloro-1-ethanenitronate present to undergo chlorination. The extent to which 10 proceeds is dependent, of course, upon the amount of 2-nitropropane in the starting material and upon the efficiency of layer separation after salt formation, as already described.

Throughout this work, vapor chromatography was used to determine composition of the chlorination products. Using a 5-meter column packed with GE-SF-96 silicone on 35/80 Chromosorb, nitromethane, nitroethane, 2-nitropropane, and 1-chloro-1-nitroethane were separated quite satisfactorily; 1,1-dichloro-1-nitroethane and 2-chloro-2-nitropropane eluted at the same time under these conditions and were therefore recorded as a single value. Since the amount of 2-nitropropane in the starting material (nitroethane) remained almost constant, it was assumed that the amount of 2-chloro-2-nitropropane in the product remained constant at 1.5% and that any increase in the combined value for the chloronitropropane and the dichloro-nitroethane above 1.5% was due to formation of the latter material. Thus, a product giving combined value of 4.0% was assumed to contain 2.5% of the dichloro compound.

Initial chlorinations were carried out on a batch basis at 0-10° in a jacketed vessel equipped with a thermocouple well, fritted tube for chlorine inlet and a bottom takeoff for product removal. Although the initial pH of the salt solution was maintained at 11.0 and no agitation was used some dichloro compound was formed. The highest quality product obtained in this system contained 92.4% 1-chloro-1-nitroethane, 0.02% nitromethane, 1.6% nitroethane, 0.38% 2-nitropropane, and 5.60% 2-chloro-2-nitropropane plus 1,1-dichloro-1-nitroethane (4.1% of the latter based on the assumption above). Apparently, under these conditions there was enough contact between the organic and aqueous phase to permit reaction 8 to occur to some extent.

Most of the chlorination studies were conducted in continuous systems. Coiled tube and straight tube reactors gave about the same results. A straight tube chlorination system is shown in Fig. 1a. Aqueous sodium ethanenitronate was metered by a proportioning pump to a pre-cooler maintained at -10 to -15°; the salt solution then entered the chlorination tube which was cooled by a brine system maintained at the desired temperature. Chlorine was fed directly to the tube through a rotameter. Effluent from the chlorinator passed to a decanter constructed to permit continuous overflow of spent aqueous layer at the top and product removal at the bottom. The pH of the spent aqueous layer was measured either directly in the decanter or in a line connected to the overflow system. When the pH of this layer was maintained at 5.5-6.5, essentially complete conversion was assured. Early in this work, no provision was made to measure the inside temperature of the chlorinator; it was assumed that it would be within 5-10° of the temperature of the circulating coolant. It was subsequently found that this was not the case and that temperatures in the reaction

zone were 30-90° higher than that of the coolant, depending on the system flow rates, chlorinator diameter, and coolant temperature. A typical profile of reaction zone temperatures as a function of residence time is shown in Fig. 2. The higher temperatures were not deleterious, provided the residence time at the higher temperature was kept to a minimum. Thus, as shown in Table 2, the purity of the chloronitroethane remained relatively constant (94.3-95.7%) over a wide range of flow rates and maximum temperatures in those cases where the residence time above 40° was less than one minute. As the time above 40° was increased to five minutes, product quality decreased rapidly to approximately 78%.

The necessity for maintaining the pH of the sodium ethanenitronate feed solution within a narrow range has been mentioned briefly. This was found to be the most critical variable in the system. As shown in Fig. 3, best results (i.e., high purity product and high conversions) were obtained in the pH range 11.0-11.15. Below this range, the conversion of nitroethane to its sodium salt is incomplete and low conversions to the chloronitroethane result. At higher pH ranges (11.3 and above) an excess of base is present, which results in conversion of 1-chloro-1-nitroethane to its sodium salt (reaction 7) and chlorination of the salt to give the dichloro compound (reaction 9). The experiments shown in Fig. 3 were carried out with slightly less (3-5%) than the theoretical amount of chlorine in the system. In subsequent work in which a slight excess of chlorine was used, total conversions above 95% and yields approaching 92% were obtained (Table 3).

Inasmuch as the chlorination reaction is quite exothermic (approximately 45 kcal/g mole), rapid heat removal in a production scale tubular reactor could not be accomplished without utilization of a complex and expensive system. This consideration led to evaluation of an agitated reaction system in order to provide rapid heat removal in a practical manner. It was feared that in an agitated system with intimate contact between organic and aqueous phases reaction 8 (salt interchange between reactant and product) would occur leading to formation of large amounts of the dichloro compound. However, when the system was investigated using a slight excess of chlorine at temperatures of 0-10°, product purity was at least as high as that produced in tubular reactors and yields were about the same. A comparison of results obtained in the two reaction systems is given in Table 3; a sketch of the agitated system is shown in Fig. 4. Apparently, the chlorination of sodium ethanenitronate proceeds at a much faster rate than salt interchange. To verify this qualitatively, a solution of 2.0 moles of 94.9% 1-chloro-1-nitroethane containing 0.17 mole of dissolved chlorine was stirred with 0.16 mole of aqueous sodium ethanenitronate for one hour at 0-10°. From the mixture, 2.13 moles of 94.8% 1-chloro-1-nitroethane were obtained, indicating the predominance of reaction 6 over 8. In a similar experiment in which the chlorine was omitted, 1.98 moles of 93.8% chloronitroethane were recovered which showed an increase of 1% in nitroethane content, indicating that reaction 8 does take place, but at a relatively slow rate.

Conversion of 1-Chloro-1-Nitroethane to 2,2-Dinitropropanol. The conversion of the chloro derivative to the alcohol was studied initially in batch runs to set conditions for a continuous process. In all work, the overall yield for the two step process was measured, since it was of interest to study the effect of variables during the ter Meer reaction on the final purity of the alcohol, as well as on yield. Conditions during the second step, the methylation reaction, were kept constant from run to run. In batch runs, 1-chloro-1-nitroethane and an aqueous solution containing sodium nitrite and potassium carbonate were fed simultaneously to a jacketed vessel containing a heel of water; the temperature was maintained in the desired range by circulation of coolant through the jacket. It was shown early in this work that an addition time of one hour and a post addition stirring period of 30-60 minutes gave the best results in batch systems. These conditions were adopted as standard procedure for the evaluation of other variables.

It has been mentioned that isolation and solvent washing of the potassium salt of 1,1-dinitroethane, the product of the ter Meer reaction, was undesirable as a purification procedure due to the impact sensitivity of the dry material. A number of alternate purification methods were investigated, as shown in Table 4. The best method found involved addition of a sufficient quantity of water to completely dissolve the salt after completion of the ter Meer reaction and removal of organic impurities by extraction of the resulting solution with ethylene chloride. The extraction was then followed by the methylation step. The yield and purity of I prepared by this method were almost identical to those obtained by the salt isolation procedure.

The effects of temperature and reactant ratios on yield were also investigated in batch runs. Temperatures of 15-20° gave best results, as shown in Fig. 5; at higher or lower temperatures, yields fell off slightly. A molar ratio of potassium carbonate/1-chloro-1-nitroethane of 1.0 gave best yields over the range studied (0.6 to 1.2), as shown in Fig. 6. An excess of nitrite ion favored high yields, as shown in Fig. 7; above a 20% excess, however, the increase in yield was slight. Thus, with molar ratios of sodium nitrite/1-chloro-1-nitroethane of 1.0, 1.2, and 1.6, overall yields of 63.7, 68.8, and 69.4% were obtained.

A continuous reaction system was constructed to operate under conditions indicated by the batch runs. The apparatus, shown in Fig. 7, was designed to carry out four steps on a continuous, integrated basis: 1) conversion of 1-chloro-1-nitroethane to the potassium salt of 1,1-dinitroethane; 2) dissolution of the salt in water; 3) extraction of the salt solution with ethylene chloride, and 4) conversion of the extracted salt solution to a solution of 2,2-dinitropropanol. The ter Meer reaction system consisted of three jacketed, cascade-type reactors connected in series so that the overflow was fed by gravity to the next reactor. Each vessel was stirred by a 2-1/4 in. diameter "Impellator" high shear stirrer at 870 rpm. The two feed streams, 1-chloro-1-nitroethane and an aqueous solution of sodium nitrite and potassium carbonate, were metered to the bottom of the first reactor (R-1) by proportioning pumps. Coolant was circulated through the reactor jackets to maintain the desired reaction temperature. The reaction product mixture overflowed the third reactor into a stirred dissolving vessel (V-1) to which water was metered to dissolve the potassium salt of dinitroethane; warm water was circulated through the jacket to maintain a temperature of 30-35°. The bottom outlet of V-1 was connected to a proportioning pump which metered this stream to the base of a modified Scheibel countercurrent extraction column. Another pump metered ethylene chloride to the top of the column to extract any unreacted 1-chloro-1-nitroethane and organic side reaction products. The column was operated so that the aqueous phase was continuous. The organic-free potassium salt solution overflowed the top of the extraction column and was mixed with a slight excess of 37% formaldehyde before entering the first stage of the methylation reactor, V-2. This vessel was equipped with a jacket, stirrer, thermometer, bottom outlet, and a dropping funnel filled with 20% sulfuric acid. Coolant was circulated intermittently as needed to maintain a temperature of 25-30°. The delivery rate of the 20% sulfuric acid was adjusted to maintain the pH at 6.8-7.0. The combined streams left this vessel by gravity flow and passed to an open-top vessel equipped with a stirrer and a side outlet near the top. Additional sulfuric acid was added to maintain the pH at 4.0 to 4.5 in this vessel. The aqueous solution of I overflowed the side outlet and was collected for isolation of product by extraction with ethylene chloride.

A series of runs was made in this system in which reactant ratios were kept essentially constant, while temperature and residence time were varied. Results, shown in Fig. 8, closely paralleled those obtained in batch studies. In the temperature range 3-25° with residence times of 0.5-2.0 hours in the ter Meer reaction, the best yield (71%) was obtained at 17° with a residence time of 1.3 hours. Data from this run are shown in Table 5. Samples were collected over 2-hour periods

beginning at 4.5 hours after system start-up. Steady state was attained in about 8 hours as judged by leveling off of product yield. The system was run for a total of 24.5 hours and gave reasonably consistent results during the period 8.5-24.5 hours. The system operated smoothly and presented no foreseeable major obstacles from the standpoint of scale-up. A number of other runs, carried out for periods of 12-26 hours, also proceeded smoothly.

COMPARISON OF METHODS

Under the best conditions for both systems, the oxidative-nitration route to 2,2-dinitropropanol gives about a 15% higher overall yield (80% vs. 65% based on nitroethane) than does the ter Meer route. Chemical costs, however, for the ter Meer process are about one-half those for the oxidative-nitration process due to silver losses, the necessity of using an expensive grade of sodium hydroxide, and the use of large quantities of nitric acid to regenerate silver nitrate. Based on these considerations, and on cost estimates for manpower and facility requirements, it appears that the oxidative-nitration process is the superior method for preparing small or intermediate quantities of 2,2-dinitropropanol, whereas the ter Meer route becomes the more economical at higher production levels.

EXPERIMENTAL

Materials. Sodium hydroxide - U.S.P., maximum chloride content 0.005%. Nitroethane - commercial grade, used as received from Commercial Solvents Corp.; the various samples used in this work averaged 93% nitroethane as determined by vapor chromatography. Potassium carbonate - commercial grade, calcinated, 99.0%. Sodium nitrite - U.S.P., granular, 99.4%. Chlorine - commercial grade obtained from The Matheson Co., 99.5%. Silver nitrate - C.P. crystals, 99.98%. Formaldehyde - commercial grade 37% aqueous solution containing 7-8% methanol. Sulfuric acid - technical grade, 98%. Nitric acid - commercial grade, 67%. Acetic acid - glacial, 99.5%. Ethylene chloride - technical grade. Methanol - commercial grade. Potassium hydroxide - technical grade, 85%. Ethyl ether - analytical reagent grade.

Analysis of nitroethane and 1-chloro-1-nitroethane. Analysis by vapor chromatography was investigated using a number of columns under several sets of conditions. Best results were obtained using a Perkin-Elmer Model 154-D Vapor Fractometer equipped with a 0.1 mv Leeds and Northrup recorder and a Perkin-Elmer Model 194 integrator. The instrument was operated at 90° with 5 meters of column packed with GE-SF-96 silicone on 35/80 Chromosorb (Wilkins Instrument and Research Co., Walnut Creek, California). A helium flow rate of 45 cc/min at 10 psig was maintained using 5 micro-liters of sample. Each major (>0.01%) component was trapped by repeatedly running samples of the crude material through the fractometer until enough material was obtained for infrared examination and for recycle to the column at a known concentration. In this manner, nitromethane (peak 3, V_R 496.8), nitroethane (peak 4, V_R 715.2), 2-nitropropane (peak 5, V_R 876.5), 1-chloro-1-nitroethane (peak 6, V_R 1235.4), 1,1-dichloro-1-nitroethane (peak 7, V_R 1498.8), and 2-chloro-2-nitropropane (peak 7, V_R 1498.8) were measured. The latter two components eluted at the same time and were calculated as a single value. Peaks 1 and 2 were present to the extent of <0.01% and were not identified.

Analysis of 2,2-dinitropropanol. A 10-g sample was weighed into a tared Erlenmeyer flask and dissolved in 50 ml of anhydrous methanol. The solution was maintained at -5 to 0°C while 50 ml of a solution containing 6.5 g of 85% potassium hydroxide in methanol was added gradually with stirring. After addition, the thick yellow slurry of potassium 1-nitro-1-ethanenitronate was stirred for an additional 2-3 minutes at -5 to 0°. The mixture was suction filtered on a sintered funnel and washed 3 times with cold anhydrous ethyl ether. When dry, the potassium salt is extremely shock sensitive (impact sensitivity of less than 5 cm using a 2-kg

weight in the Bureau of Mines apparatus) and should be kept damp with solvent during handling operations. After the last ether wash, the salt was transferred (behind a safety shield) to a tared Petri dish and spread as thin as possible. The dish was placed on a balance and solvent allowed to evaporate until constant weight was reached. The sample was safely disposed of by quenching with water before removal from the balance.

Preparation of 2,2-dinitropropanol by the oxidative-nitration method. A suspension of nitroethane (150 g, 93% purity, 1.86 moles) and water (400 ml) was stirred vigorously while a solution of 50% sodium hydroxide (168 g, 2.1 moles) was added over a 25-min period while keeping the temperature at 0-10°. After addition was complete, sodium nitrite (144 g, 2.1 moles) was added and the mixture was stirred an additional 5-10 min. The mixture was added, over a 2-min period, to a vigorously agitated solution of silver nitrate (644 g, 3.8 moles) in 2400 ml of water which had been precooled to 0°. Two minutes after addition, the temperature had risen to 12° and the pH was 5.0. After stirring an additional 30 min at 10-15°, the mixture was treated with 50% sodium hydroxide, added over a 25-min period at 10-20°, until a pH of 12-13 was reached. The mixture was filtered and the silver washed three times with 400-ml portions of water. The pH of the combined filtrates was adjusted to 8.5-9.5 with acetic acid, and 37% formaldehyde (170 g, 2.1 moles) was added all at once. The pH was then adjusted to 5.0 with acetic acid at 20-25° over a 30-min period. After stirring an additional 30 minutes, the solution was extracted eight times with 400-ml portions of ethylene chloride. Removal of the solvent in vacuo left 230 g of 97% 2,2-dinitropropanol; overall yield, 79.9% based on the nitroethane content of the starting material.

Conversion of recovered silver to silver nitrate. Recovered silver (454 g) was slurried with 350 ml of water in a reaction vessel equipped with a caustic scrubbing system to remove oxides of nitrogen. With good stirring, 67% nitric acid (640 g) was added over a 4-hr period at 30-40°. Stirring was continued after addition for 1 hr at 40° and the pH of the solution was then adjusted to 5.0-5.5 by gradual addition of 50% sodium hydroxide.

Preparation of sodium ethanenitronate for chlorination studies. (a) Batch procedure. To a precooled and vigorously stirred mixture of 92.6% commercial nitroethane (900 g, 11.08 moles) and 1800 ml of water, 35.85% sodium hydroxide (1275 g, 11.11 moles) was added at 5-10° in 15 min. The mixture was stirred an additional 15 min, diluted to 4 liters, and transferred to a separatory funnel where the unreacted organic layer (the majority being 2-nitropropane) was separated. The lower aqueous layer was stored at 5° prior to use. The final solution contained 23.45% sodium ethanenitronate and had a pH of 10.6-11.0. (b) Continuous procedure. Continuous reactions were carried out in a two stage cascade reaction system (Fig. 1) equipped with paddle agitators and jackets through which coolant was circulated. Equimolar streams of 15% sodium hydroxide and nitroethane were fed to the first 400-ml reactor by proportioning pumps. The stage heights were arranged to permit gravity overflow from the first stage to the bottom of a second identical reactor. The product overflowing the second reactor was fed to a decanter for separation of unreacted 2-nitropropane from the aqueous product solution.

Conversion of sodium ethanenitronate to 1-chloro-1-nitroethane. (a) Tube chlorinator. A sketch of the tube chlorination system is shown in Fig. 1a; the reactor was a jacketed tube 1 cm I.D. x 72 cm long and was equipped with a thermocouple well which extended the length of the tube. Precooled aqueous sodium ethanenitronate and chlorine were fed to the tube inlet through a proportioning pump and a rotameter, respectively. Coolant, at the desired temperature, was circulated through the tube jacket. Effluent from the tube flowed to a decanter where the pH of the spent aqueous layer was measured. (b) Stirred chlorinator. The stirred chlorination system is shown in Fig. 4. The reactor (2.54 cm I.D. x

28 cm height) was equipped with a jacket for coolant circulation, thermocouple well, and paddle stirrer. Precooled aqueous sodium ethanenitronate was fed to the top of the reactor by a proportioning pump; chlorine was fed to a bottom inlet through a rotameter. The product mixture flowed by gravity to a decanter where the spent aqueous and organic layers were separated continuously. The pH of the aqueous layer was measured in the decanter. After separation of the crude product, it was dried with sodium sulfate (3 g per 100 g of crude product) and filtered before analysis. Yields were based on the amount of dried, filtered material recovered. When an excess of chlorine was used, a stream of air was blown through the crude material to remove dissolved chlorine before the drying step.

Batch conversion of 1-chloro-1-nitroethane to 2,2-dinitropropanol. Typical run. A solution of potassium carbonate (138 g, 1.0 mole) and sodium nitrite (82.8 g, 1.2 mole) in 500 ml of water was added simultaneously with 95% 1-chloro-1-nitroethane (109.5 g, 0.95 mole) over a 1-hr period to a vigorously stirred 100 ml heel of water at 12-18°. After the addition, the slurry of precipitated yellow potassium salt of 1,1-dinitroethane was stirred 30 min at 12-18°. The salt was dissolved at 25° by addition of 1400-1700 ml of water, and the resulting solution extracted twice with 300-ml portions of ethylene chloride. The aqueous layer was treated with 37% formaldehyde (60.4 g, 0.745 mole) and the solution acidified, over a 30-min period, to pH 4.0-4.5 with 400-500 g of 20% sulfuric acid. The solution was allowed to stir another 30 min and was then extracted with 12 aliquots of 150 ml of ethylene chloride. The combined organic extracts were stripped in vacuo to leave 100.6 g of 99.0% 2,2-dinitropropanol; overall yield, 69.9% based on the 1-chloro-1-nitroethane content of the starting material.

Continuous conversion of 1-chloro-1-nitroethane to 2,2-dinitropropanol. The apparatus employed in these studies is shown in Fig. 8. 1-Chloro-1-nitroethane (94-96% purity) and aqueous feed (1.2 moles of sodium nitrite and 1.0 mole of potassium carbonate per 600 ml of water) were metered separately to the first stage reactor of the ter Meer reaction system by proportioning pumps. Rates were adjusted to maintain a molar feed ratio of $\text{CH}_3\text{CHClNO}_2/\text{NaNO}_2/\text{K}_2\text{CO}_3 = 0.95/1.2/1.0$ and a total residence time of 0.5-2.0 hr in the three stage reaction system. The "Impellator" stirrers in each reactor were adjusted to a rate of 870 rpm. Temperature was controlled in the desired range by circulation of coolant through the reactor jackets; maximum temperature spread through the three stages was 3°. The potassium salt product slurry overflowed the third stage to a dissolving vessel to which water (2000 ml/mole of 1-chloro-1-nitroethane fed) was pumped; temperature was maintained at 30-35° by circulation of water through the jacket. The resulting potassium salt solution was pumped to the base of a modified Scheibel column. Ethylene chloride (1000 ml/hr in all runs) was pumped to the top of the column. The extracted aqueous effluent from the column was allowed to flow by gravity to a jacketed reaction vessel to which 37% formaldehyde (0.85 mole/mole of 1-chloro-1-nitroethane fed) and 20% sulfuric acid were added; pH in this reactor was maintained at 7.0-7.5 and the temperature at 25-30°. Effluent from this reactor was allowed to flow to a second vessel in which the pH was maintained at 4.0-4.5 by further addition of 20% sulfuric acid. Effluent from this reactor, containing about 3% 2,2-dinitropropanol, was collected as product. A complete weight balance was conducted for each sample. Aliquots (4 liters) of each sample were extracted twelve times with 300-ml portions of ethylene chloride; solvent was then removed in vacuo in a rotary evaporator with final heating of the residue at 45°/0.1 mm for 1 hr. Phase distribution studies showed that the extraction procedure described above gave a 96% recovery of product from the aqueous layer. Continuous extractions in the modified Scheibel column gave a 94% average recovery.

TABLE 1

TYPICAL ANALYSIS OF 2,2-DINITROPROPANOL PREPARED VIA THE
OXIDATIVE-NITRATION REACTION

2,2-Dinitropropanol	97.0
Mononitro Compounds*	2.0
1,1-Dinitroethane	0.5
Formaldehyde	0.1
Silver	0.05
Water	0.1
Acetone Insolubles	0.1

*Includes nitroethane, 2-nitro-1-propanol and
2-nitro-2-methyl-1,3-propanediol

TABLE 2

EFFECT OF RESIDENCE TIME ABOVE 40°C ON THE PURITY OF
1-CHLORO-1-NITROETHANE

Run No.	Residence Time in Chlorinator, min.		Maximum Temp., °C	Mole % in Product	
	Total	Above 40°C		1-Chloro-1- Nitroethane	2-Chloro-2-Nitropropane 1,1-Dichloro-1-Nitroethane
1	1.35	0.31	68	95.7	1.50
2	1.72	0.30	58	94.8	2.34
3	3.70	0.52	58	95.6	1.86
4	4.88	0.00	39	95.7	1.87
5	6.90	0.73	50	95.5	2.50
6	10.40	0.55	50	94.3	2.39
7	17.50	1.23	50	92.5	3.70
8	9.90	5.57	76	78.5	8.65 ^a
9	5.22	5.22	70	77.3	10.90 ^b

^aAlso contained 11.9% nitroethane.

^bAlso contained 10.6% nitroethane.

TABLE 3
RESULTS IN TUBE AND STIRRED CHLORINATORS

Run	pH of Sodium Ethanimpropanol Feed	Residence Time, min.		Type Reactor	% Yield	Product Analysis, Mole %				
		Total	Above 40°C			Nitro- methane	Nitro- ethane	2-Nitro- propane	1-Chloro-1- Nitroethane	1,1-Dichloro-1- Nitroethane + 2-Chloro-2- Nitropropane
1	11.0	3.70	0.520	Straight Tube	84.0 ¹	.130	1.16	1.07	95.62	1.86
1	10.7	6.90	0.740	"	87.0	.070	1.30	0.46	95.63	2.44
2	10.8	1.13	0.395	"	90.7	.075	1.65	1.25	95.06	1.97
3	11.0	9.45	0.2	Stirred	.28	2.15	0.34	0.94	95.22	1.72
4	11.1	9.7	0.2	"	90.5	.23	0.86	1.09	95.81	1.74
5	11.0	17.8	0.2	"	89.5	.09	0.94	1.00	95.54	2.30
6	10.9	40.6	0.2	"	87.3	.06	1.57	0.77	95.51	2.04

¹ pH of aqueous effluent maintained at 7.4-7.7; in all other runs the pH was maintained at 5.5-6.5. ² Temperature maintained at 0-10°.

TABLE 4
PURIFICATION PROCEDURES FOR 2,2-DINITROPROPANOL PREPARED BY THE TER MEER REACTION

Run	Procedure	2,2-Dinitropropanol	
		% Yield	% Purity
1	Potassium salt of 1,1-dinitroethane filtered and washed with methanol before methylation step.	69.4	99.2
2	Aqueous 2,2-dinitropropanol product solution extracted with <u>n</u> -hexane before isolation of product by ethylene chloride extraction.	67.7	93.4
3	Same as Run 2 except for substitution of cyclohexane for <u>n</u> -hexane.	71.3	95.8
4	Same as Run 2 except for substitution of toluene for <u>n</u> -hexane.	63.7	98.2
5	Dissolved potassium salt of 1,1-dinitroethane in water and extracted with methylene chloride before methylation step.	58.3	98.0
6	Same as Run 5 except for substitution of ethylene chloride for methylene chloride.	68.8	99.6

TABLE 5
DATA ON CONTINUOUS CONVERSION OF 1-CHLORO-1-NITROETHANE TO 2,2-DINITROPROPANOL

Run & Sample	Sample Period, Hr.	Molar Feed Ratio $\frac{\text{CH}_3\text{CHClNO}_2}{\text{NaNO}_2/\text{K}_2\text{CO}_3}$	Ter Meer Residence Time, Hr.	Ter Meer Reaction Temperature, °C			Total wt. Balance, %	$\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_2\text{OH}$ Assay, %	Yield %
				R-1	R-2	R-3			
15-A*	4.5-6.5	0.938/1.2/1.0	1.30	17.0	15.0	14.3	100.9	98.7	68.4
15-B*	6.5-8.5	0.938/1.2/1.0	1.305	17.0	15.0	14.3	99.8	98.5	68.5
15-C	8.5-10.5	0.953/1.2/1.0	1.305	17.2	15.1	14.6	94.8	99.4	70.8
15-D	10.5-12.5	0.960/1.2/1.0	1.31	17.1	15.1	14.5	101.2	98.2	69.7
15-E	12.5-14.5	0.968/1.2/1.0	1.305	17.1	15.1	14.5	95.3	98.8	70.0
15-F	14.5-16.5	0.953/1.2/1.0	1.30	17.1	15.1	14.5	98.4	99.2	69.4
15-G	16.5-18.5	0.938/1.2/1.0	1.295	17.0	15.0	14.6	99.0	98.8	71.6
15-H	18.5-20.5	0.930/1.2/1.0	1.30	17.0	15.0	14.6	99.4	99.3	74.0
15-I	20.5-22.5	0.938/1.2/1.0	1.305	17.0	15.0	14.6	99.4	98.8	72.8
15-J	22.5-24.5	0.938/1.2/1.0	1.31	17.0	15.0	14.6	96.3	99.1	69.9
Average							98.4	98.9	71.0

* Not steady state (not included in average).

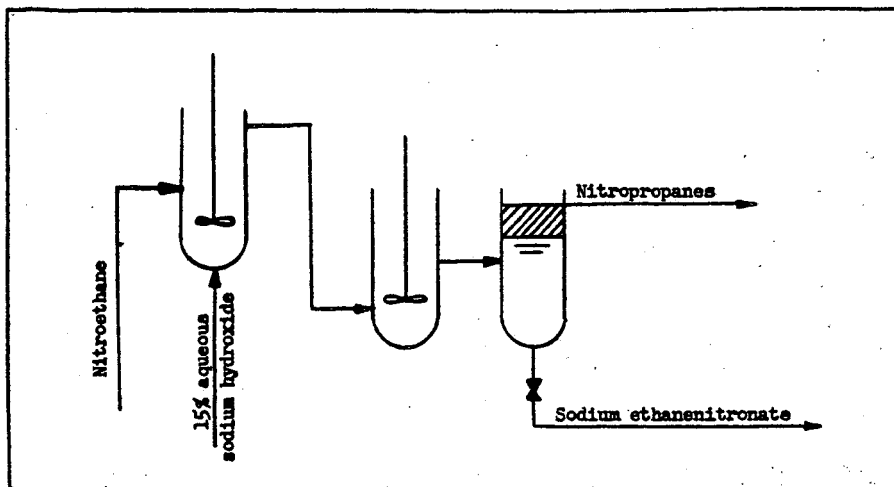


Figure 1. Reaction system for the continuous preparation of sodium ethanenitronate from nitroethane.

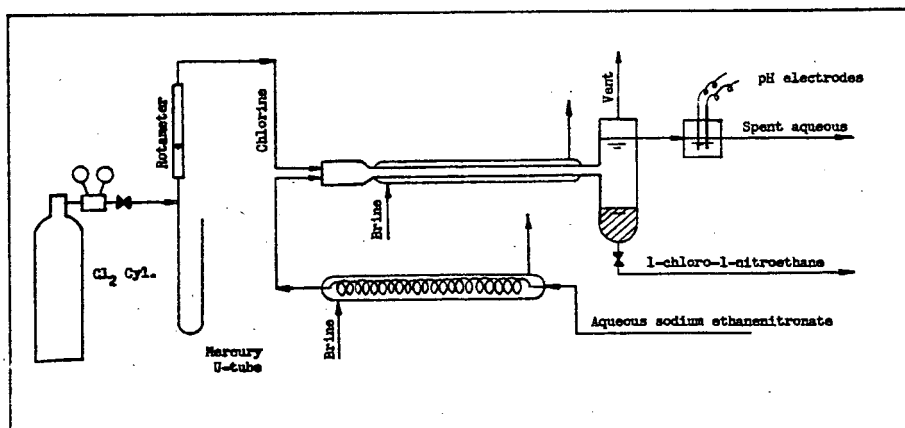


Figure 1a. Straight tube reactor system for the continuous conversion of sodium ethanenitronate to 1-chloro-1-nitroethane.

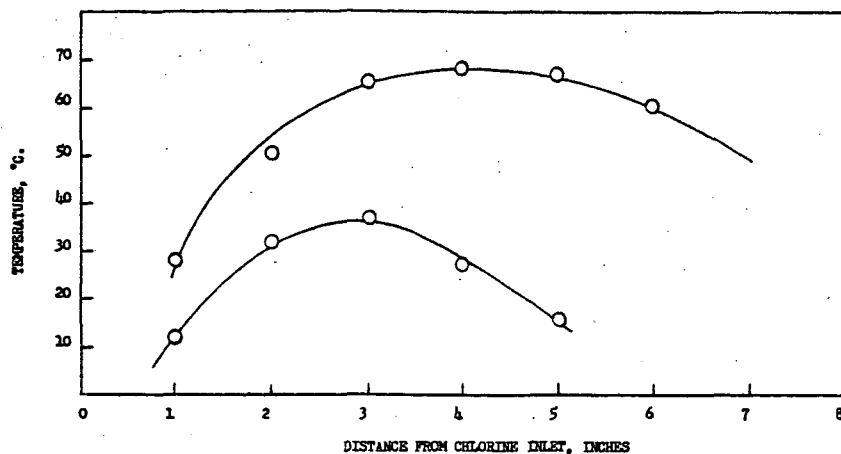


Figure 2. Reaction temperature profiles in straight tube chlorinator. Reactor length 28.4 inches. Sodium ethanenitronate concentration 2.76 m/l. Total residence times: A = 4.05 min., B = 1.35 min.

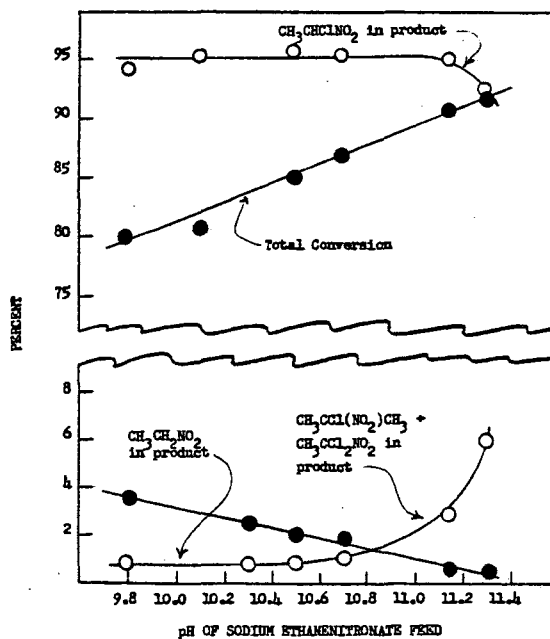


Figure 3. Effect of pH on conversion and product purity in continuous coiled tube reactor. Residence time 7 minutes.

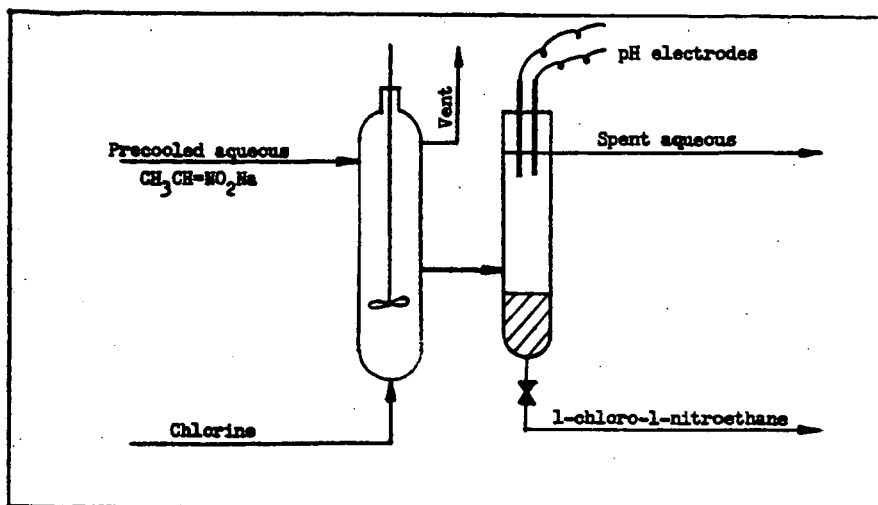


Figure 4. Agitated reaction system for the chlorination of sodium ethanenitronate.

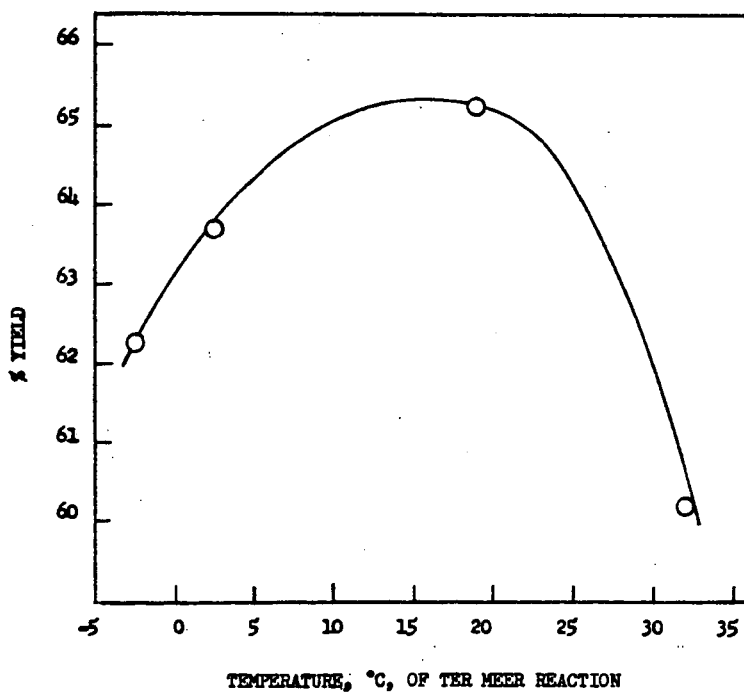


Figure 5. Effect of temperature during ter Meer reaction on 2,2-dinitropropanol yield in batch reactor. $\text{NaNO}_2/\text{K}_2\text{CO}_3/\text{CH}_3\text{CHClNO}_2$ molar ratio = 1.0/1.0/1.0.

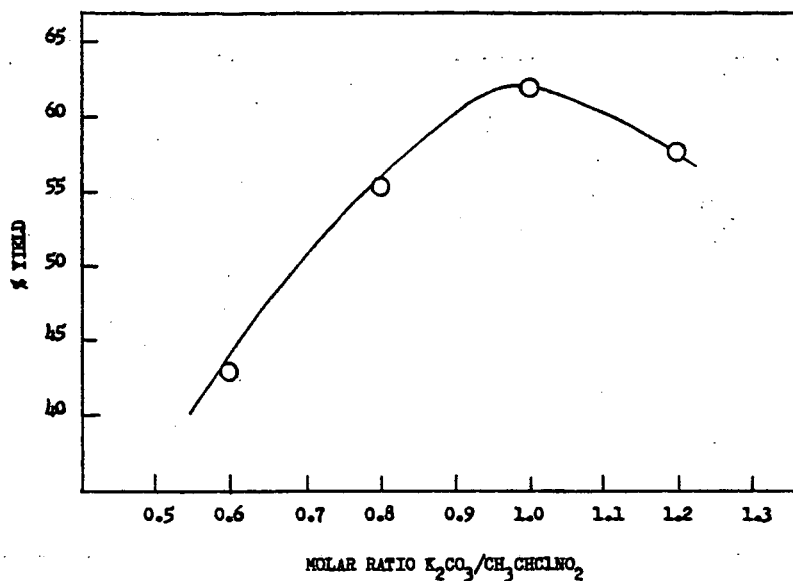


Figure 6. Effect of reactant ratios on 2,2-dinitropropanol yield in ter Meer reaction at 0 - 10°C in batch reactor. Molar ratio $NaNO_2/CH_3CHClNO_2 = 1.0$.

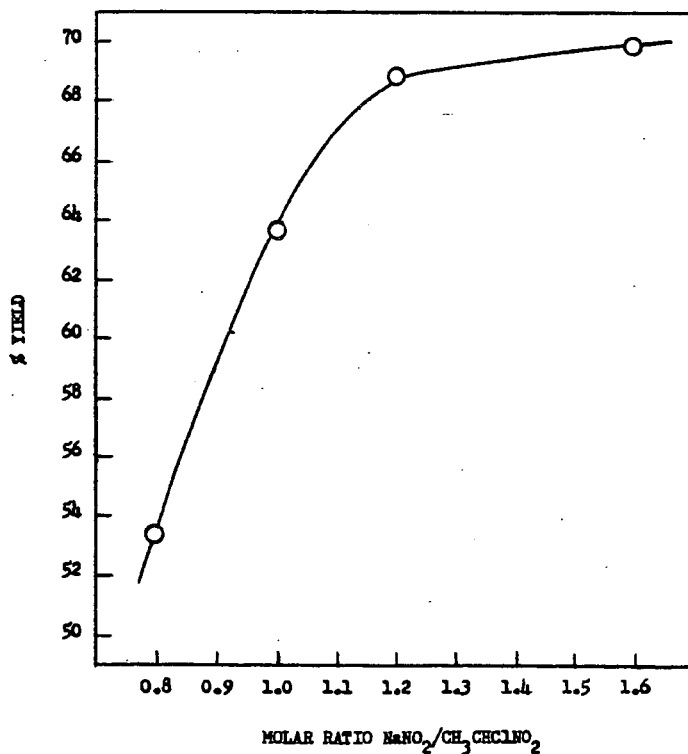


Figure 7. Effect of reactant ratios on 2,2-dinitropropanol yield in ter Meer reaction at 0 - 10°C in batch reactor. Molar ratio $K_2CO_3/CH_3CHClNO_2 = 1.0$.

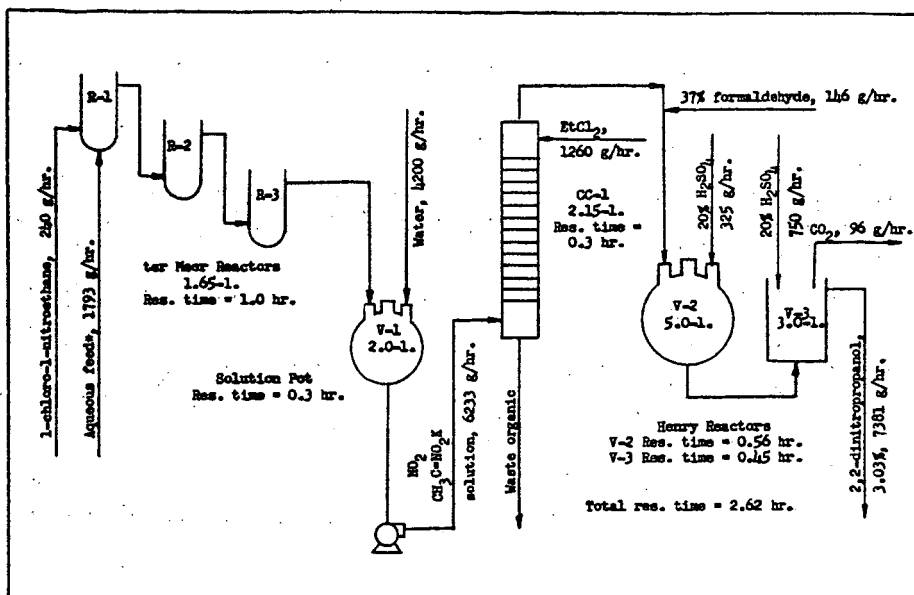


Figure 8. Reaction system for continuous preparation of 2,2-dinitropropanol from 1-chloro-1-nitroethane. Aqueous feed was prepared by dissolving 83 g. HNO_3 (1.2 mol.) and 138 g. K_2CO_3 (1.0 mol.) per 600ml. water.

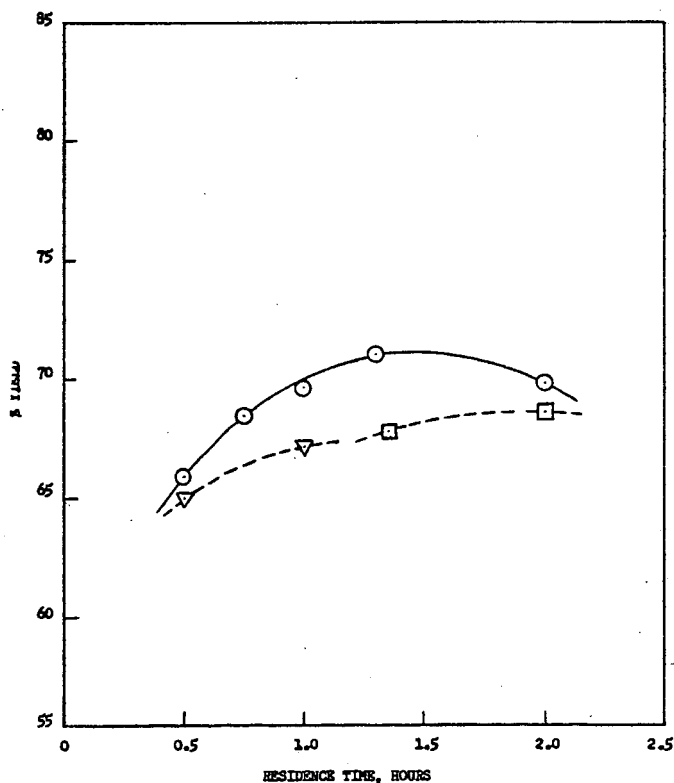


Figure 9. Effect of residence time on the yield of 2,2-dinitropropanol from 1-chloro-1-nitroethane via the ter Meer Reaction. Reaction temperature: □ = 3°C, ○ = 17°C, and ▽ = 25°C.

REFERENCES

- (1) L. Henry, Compt. rend., 120, 1265 (1895)
- (2) R.B. Kaplan and H.O. Shechter, "A New General Reaction for Preparing gem-Dinitro Compounds." Paper No. 1, Symposium on Nitro Aliphatic Chemistry, Purdue University, May 25-26, 1961.
- (3) S.B. Lippincott, J. Am. Chem. Soc., 62, 2604 (1940); U.S. Patent 2,260,256, Oct. 21, 1941.
- (4) C.M. Wright and D.R. Levering, "Electrolytic Preparation of gem-Dinitro-paraffins." Paper No. 2, Symposium on Nitro Aliphatic Chemistry, Purdue University, May 25-26, 1961.
- (5) E. ter Meer, Ann. 181, 1 (1876)
- (6) L.G. Maury and D.R. Levering, Hercules Powder Co., Private Communication.